THE PRECIPITATION AND TITRATION OF MAGNESIUM OXYQUINOLATE IN THE PRESENCE OF CALCIUM OXALATE, AND ITS APPLICATION IN THE ANALYSIS OF PORTLAND CEMENT AND SIMILAR SILICATES

By John C. Redmond

ABSTRACT

Data are presented showing that magnesium oxyquinolate can be precipitated and titrated in the presence of calcium oxalate. A rapid method for the determination of magnesium in portland cements is described.

CONTENTS

I. INTRODUCTION

A rapid and accurate method for the determination of magnesia in portland cements and similar materials by the use of 8-hydroxy-quinoline was described by Redmond and Bright (3)[1] in 1931. In this procedure, which has been in use for the routine analysis of portland cements at the Bureau of Standards for several years, the sample is dissolved in dilute hydrochloric acid, the R_2O_3 group and calcium are removed as usual, and magnesium then determined by precipitating with 8-hydroxyquinoline (1), dissolving the precipitate in acid, and titrating with a standard bromate solution. The work reported in this paper demonstrates that this method can be further shortened by omitting the removal of the calcium oxalate and precipitating and titrating the magnesium oxyquinolate in the presence of the calcium oxalate.

Shead and Valla (4) claim that magnesium oxyquinolate can be precipitated in the presence of calcium oxalate. In their method the combined precipitates of calcium oxalate and magnesium oxyquinolate are ignited, weighed, and lime subsequently determined by the

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[1] The figures given in parentheses here and throughout the text relate to the reference numbers in the bibliography given at the end of this paper.

saccharate method. Bucherer and Meier (2) have described a method wherein the magnesium oxyquinolate is precipitated in the presence of calcium oxalate, and magnesium determined by their "filtration method." A brief description of the experimental work showing that the precipitated magnesium oxyquinolate can be titrated in the presence of calcium oxalate, together with complete directions for the application of the method in the analysis of portland cements, are given in the following sections. By using the method described, an experienced operator can determine magnesia in a portland cement or limestone in 1 to 1½ hours.

II. EXPERIMENTAL

Solutions of pure salts of magnesium, calcium, iron, and aluminum were used to obtain the various quantities of these elements present in the different test solutions. The procedures for separating magnesium from the several elements, and its precipitation and titration as the quinolate are given in section III.

Preliminary experiments showed that calcium once precipitated as the oxalate does not retain any 8-hydroxyquinoline, and that the presence of oxalic acid has no observable effect on the titration of 8-hydroxyquinoline with standard bromate and thiosulphate solutions. Further experiments showed that calcium must be precipitated as the oxalate, for otherwise more or less of it reacts with 8-hydroxyquinoline and precipitates as oxyquinolate with the magnesium. For instance, aliquot portions of solutions of magnesium chloride containing 0.0247 g of MgO indicated 0.0252, 0.0255, and 0.0270 g when adulterated with 0.0010, 0.0043, and 0.0300 g of CaO, respectively. Incidentally it was noted that the presence of iron or aluminum hydroxide causes errors in the precipitation and titration of magnesium oxyquinolate.

The results obtained by precipitating calcium as the oxalate and then precipitating magnesium in the presence of the calcium oxalate, dissolving the precipitate in hydrochloric acid, and titrating with a solution of bromate are shown in table 1. Each result is the average of two or more closely agreeing determinations. Two different methods were used to precipitate the calcium. In one case hot ammonium oxalate solution was added to a boiling faintly ammoniacal solution of the calcium and magnesium, and in the other case a boiling acid solution containing the magnesium and calcium, together with oxalic acid, was made ammoniacal by the dropwise addition of concentrated ammonia. The data show that for moderate amounts of lime and magnesia the results are sufficiently accurate for routine work. For high quantities of lime and magnesia the usual occlusion of magnesia that occurs when calcium oxalate is precipitated only once takes place no matter whether the calcium is precipitated in acid or ammoniacal solution. The addition of the 8-hydroxyquinoline prior to the calcium precipitation does not inhibit the occlusion of magnesia, for the results obtained are the same as when the reagent is added after the calcium precipitation.

TABLE 1.—*Results obtained by the precipitation of magnesium oxyquinolate in the presence of calcium oxalate*

Experiment no.	CaO taken	MgO taken	MgO found	Error	Remarks
	g	*g*	*g*	*g*	
1	0.034	0.0147	0.0146	−0.0001	Calcium oxalate precipitated in ammoniacal solution.
2	.060	.0147	.0148	+.0001	Calcium oxalate precipitated from acid solution by adding ammonia.
3	.170	.0195	.0194	−.0001	Same as in experiment 1.
4	.170	.0242	.0240	−.0002	Do.
5	.170	.0242	.0240	−.0002	Same as in experiment 2.
6	.300	.0049	.0049	.0000	Same as in experiment 1.
7	.300	.0147	.0144	−.0003	Same as in experiment 2.
8	.300	.0244	.0239	−.0005	Same as in experiment 1.
9	.300	.0244	.0236	−.0008	Same as in experiment 1, but calcium oxalate filtered before precipitating Mg.
10	.300	.0244	.0237	−.0007	Same as in experiment 1, 8-hydroxyquinoline added before oxalate precipitation.

The data given in table 2 were obtained by applying the recommended procedure to synthetic solutions which had been made to approximate solutions obtained from 0.5 g samples of portland cements. These solutions contained 0.020 g of Al_2O_3, 0.008 g of Fe_2O_3, 0.300 g of CaO, and the amounts of MgO shown in the table. The errors are no greater than are obtained in any procedure involving single precipitations with ammonium hydroxide and with ammonium oxalate, and are within commercial tolerances. By repeating the precipitation of the ammonium hydroxide group and of the calcium oxalate more accurate results can be obtained.

In addition to the data given in table 2, 0.8 g samples of Bureau of Standards standard sample of argillaceous limestone no. 1a (certificate value 2.19 percent MgO) were ignited for 30 minutes at 1,100° C. and magnesia was then determined by the recommended method. An average value of 2.14 percent magnesia was obtained.

TABLE 2.—*Results obtained for MgO in synthetic solutions of cement*

Experiment no.	MgO	
	Present	Found
	Percent	*Percent*
11	1.96	1.96
12	3.90	3.82
13	4.88	4.72
14	4.88	[1] 4.84

[1] R_2O_3 and CaO reprecipitated.

III. RECOMMENDED METHOD FOR THE RAPID DETERMINATION OF MAGNESIA IN PORTLAND CEMENT

1. SOLUTIONS REQUIRED

The solutions used in this procedure and their methods of preparation are those described by Redmond and Bright (3), with the exception of the method of standardization of the bromate-bromide solution. This is made as follows: To 200 ml of water in a 400-ml beaker add exactly 25 ml of the potassium bromate-potassium-bromide solution (0.2 N). Add 20 ml of hydrochloric acid (specific gravity

1.18), stir, and add immediately 10 ml of potassium iodide solution (25 percent). Mix well, and titrate at once with standard sodium thiosulphate solution (0.1 N) until nearly colorless. Add 2 ml of starch solution and titrate to the disappearance of the blue color.

2. PROCEDURE

To a 0.500 g sample in a 400-ml beaker add 10 ml of water and 10 ml of hydrochloric acid (specific gravity 1.18). Heat gently and grind any coarse particles with the flattened end of a glass rod until decomposition is complete. Dilute to 150 ml with hot water.

To the solution add three drops of methyl red (0.02 percent alcoholic solution), and then ammonium hydroxide (specific gravity 0.90) until the solution is distinctly yellow. Add macerated filter paper, and heat to boiling. Boil from 1 to 2 minutes, remove from the hot plate, and allow to stand until the precipitate has settled. Filter without delay, and wash the precipitate with a hot 2 percent solution of ammonium chloride. To the filtrate add 1 ml of ammonium hydroxide (specific gravity 0.90), and heat to boiling. When boiling, add 25 ml of a hot 4 percent solution of $(NH_4)_2CO_4.H_2O$ and continue boiling for 2 minutes. Digest on the steam-bath for 10 to 15 minutes.

Cool the solution to 70° C., add 20 ml [2] of a clear 1.25 percent solution of 8-hydroxyquinoline (25 g of the reagent dissolved in 60 ml of glacial acetic acid and diluted to 2 liters with water), and then 4 ml of ammonium hydroxide (specific gravity 0.90) per 100 ml of solution. Stir on a mechanical stirring machine for 15 minutes, and set aside until the precipitate has settled. Filter, and wash with hot dilute ammonium hydroxide (1 + 40). Dissolve the precipitate in 50 to 75 ml of hot dilute hydrochloric acid (1 + 9), dilute the resulting solution to 200 ml, and add 15 ml of hydrochloric acid (specific gravity 1.18). Cool to 25° C., and add from a pipette 25 ml of standard bromate-bromide solution (0.2 N). Stir and let stand for about 30 seconds to insure complete bromination. Add 10 ml of potassium iodide solution (25 percent), stir well, and then titrate with standard sodium thiosulphate solution (0.1 N) until the color of the iodine becomes faintly yellow. At this point add 2 ml of starch solution and titrate to the disappearance of the blue color.

The percentage of magnesia in a 0.5 g sample may be calculated as follows:

A = g of MgO per ml of standard sodium thiosulphate solution.

B = ml of standard sodium thiosulphate solution equivalent to 25 ml of standard bromate solution.

C = ml of sodium thiosulphate solution required in the titration.

Then

$(B - C) \times A$ = g of MgO.

g of MgO $\times 200$ = percent of MgO.

IV. LITERATURE CITED

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3. Redmond, J. C., and Bright, H. A., B.S. Jour. Research, vol. 6, pp. 113–120, 1931.
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[2] This amount suffices for 0.5 g samples containing 6 percent or less of magnesia. For cements of higher magnesia content proportionately more reagent should be added.